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PROCESSING MECHANISMS, STRUCTURE AND MORPHOLOGY OF HIGH TEMPERATURE POLYMERIC ALLOYS

CELANESE CORPORATION
CELANESE RESEARCH COMPANY
SUMMIT, NEW JERSEY 07901

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(Block #20)

In the initial phase of this project the processing conditions expected to
optimise interactions at a molecular level between poly (bisbenzimidazo-
benzophenanthroline) (BBB) and polybenzimidazole (PBI) were investigated.
Studies of the mechanical properties and the morphology indicate that
binary interactions between BBB-BBB, PBI-PBI and BBB-PBI all occur.
Interactions of BBB-BBB occur at temperatures above 500°C while PBI-PBI
and BBB-PBI interactions occur at lower temperatures. Separation of
these interactions should be possible by varying the processing conditions
between temperatures of 350° and 550°C and by using a range of composites
prepared both by dry-blending and co-precipitation of the two polymers.

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SECTION I

INTRODUCTION

A. Historical

Continuing advances in aerospace missile and weapons technology
have created a growing demand for high-temperature lightweight
materials. In meeting such a demand, research chemists have
synthesized a substantial number of new polymer systems, many
of which indeed possess a remarkable degree of thermal stability.
Among these are several highly condensed, heterocyclic polymers,
including polyimidazopyrrolones (pyrrones) and poly (bisbenzimi-
dazobenzophenanthrolines) (BBB and BBL), the so-called "ladder"
polymers.

Regrettably, some of the most stable systems have proved to be
difficult to process into useful forms by currently available
fabricating techniques, even at prepolymer stages. Thus, although
BBB polymers, for example, can be converted into continuous
fibers [1], they defy shaping by conventional molding and extru-
sion processes.

In recognition of the problem, the Air Force Materials Laboratory
(AFML) mounted an exploratory development effort directed toward
finding new methods to process high Tg polymers of the BBB type.
Celanese was selected in a competitive solicitation by AFML to
carry out the project.

In the course of working on contract F33615-72-C-1642, Celanese
investigators studied [2] the processability of different molecular
weight BBB polymers by hot pressing the material, as-received
or modified in various ways, under different conditions and chara-
cterizing the formed specimens by suitable analytical techniques.
The BBB polymer can be densified without additives to over 94%
of true density by hot pressing at about 500°C and 50,000 psi
pressure, but the strength of the molded piece is low. Addition
of BBB precursor monomers as binders and chopped BBB fibers
as reinforcement yielded molded pieces with a slightly higher
flexural strength, but the temperature and pressure conditions
remained beyond those in industrial practice.

It was found toward the end of the contract period that the addition
of polybenzimidazole (PBI) polymer was most effective in yielding
a well-consolidated specimen at lower temperatures and pressures,

1.

but the contract ended before this observation could be fully explored. Among other accomplishments made under the contract, the Celanese researchers showed that the thermo-- mechanical analysis (TMA) thermograms correlate with the processing temperature and state of purity of the BBB polymer and these are useful in identifying potential plasticizing additives. A procedure for fabricating fiber reinforced BBB matrix pre- preg plies was partially developed but well-consolidated laminates were not achieved.

Subsequent to the completion of the AFML contract, Celanese, with its own corporate funds, supported additional experimental work to confirm and verify the observation that mixtures of BBB and PBI polymers are more tractable and processable than is BBB by itself. On the basis of these results and observations, Celanese Research Company submitted an unsolicited proposal to AFOSR to study the mechanism of the improved processability of BBB/PBI polymer alloys and related systems[3]. This proposal was funded by AFOSR under contract No. F49620-77-C-0046 and is the subject of this report.

The work on this project was considered to fall into two categories: firstly, to confirm and expand the earlier results obtained at Celanese and with regard to the effect of processing conditions on properties in order to define the conditions under which a max- imum response should be observed; and, secondly, to obtain a basic understanding of the microscopic changes which give rise to the improved processability. To this end, the initial effort was directed at exploring a range of processing variables using the change in mechanical properties as a principal means of charac- terization. Changes in morphology were also followed using a variety of microscopical techniques. Studies of the effects occurring on a molecular level were postponed until an optimum processing condition had been defined.

B. Statement of Work

The work, as set forth in this report, was guided by the Statement of Work which is part of Contract F49620-77-C-0046:

1. The contractor will study the processability of intractable polymers, such as, but not limited to BBB, when alloyed with compatible polymers and monomers, such as, but not limited to PBI polymer and BBB monomers.

2.

2. The contractor will utilize his capabilities and experience in
the chemistry and physics of polymers to investigate the
particulate form and character of polymer mixtures before
hot pressing and correlate these with physical and mechanical
properties after consolidation. To the extent that it is desirable,
statistically designed experiments will be used to define critical
variables. To examine physical changes which occur before
and after consolidation, appropriate microscopic techniques
will be employed.

3. The contractor will consider several approaches to establish
the presence or absence of changes in chemical bonding occurring
during processing. Fourier-Transform infrared spectroscopy,
thermal-spectrometric analysis and electron-proton resonance
analysis are representative of techniques expected to yield infor-
mation relating to the chemical nature of the polymer alloys.

4. Interim reports detailing the progress of the work will be sub-
mitted on an annual basis. At the completion of the project a
final scientific report will be delivered.

SECTION II

EXPERIMENTAL

A. Materials

Samples of BBB and PBI polymers were furnished by Celanese Research Company at no direct cost to the project. The BBB used had the identification 22323-30 and was in the form of coarse flakes. Two PBI samples were used with different inherent viscosities (I.V.). The lower I.V. sample (#26184-12) was in the form of a fine powder. While the other (#P6915A) had a larger particle size in which agglomeration had occurred to form large lumps.

The coarse nature of both the BBB and the higher I.V. PBI made them unsuitable for blending as is and the particle size was reduced by cryogenic grinding using a Mikro-Pulverizer hammer mill. The grinding procedure used was to pre-cool both the polymer and the mill with liquid nitrogen and then to feed a mixture of polymer and liquid nitrogen slowly into the grinder. Two passes were made. The first pass used a 20-mil herring bone screen, the second, a 10-mil screen. After grinding, the polymer was vacuum dried at 150°C for 12 hours.

The polymers were characterized for I.V. and surface area before and after grinding (Table I). The I.V. was measured in 97% H_2SO_4 using a concentration of 0.2% for the BBB and 0.4% for the PBI. Specific surface areas were measured by the BET method using a Quantisorb Surface Area Analyzer. Particle size analysis was carried out on a Quantimet Image Analyzer using the longest dimension of each particle for characterization. Apparent and tap densities were also measured using methods similar to the ASTM Standard Methods B417 and B527. These results are also listed in Table I.

The high surface area, large particle size and low apparent density value, taken together, suggest that the BBB powder particles are highly porous and hence, the change in surface areas during grinding, could be due to compaction of the particles. Scanning and transmission electron microscopy (SEM and TEM) of the untreated BBB also indicate that this sample is very porous (Figures 1a and 1b). This may be deduced, for example, in Figure 2, where the white areas are voids, the dark areas BBB.

The low surface area of the 0.90 I.V. PBI and the scanning electron micrograph (Figure 2a) show that the particles of this polymer are much more compact. The small change in I.V. on grinding is not considered to be significant. The 0.59 I.V. material, however, again has a somewhat

4.

TABLE I.

CHARACTERIZATION OF POLYMER POWDERS USED FOR BBB/PBI BLENDS

Polymer	Lot #	Inherent Viscosity (dl/g)		Surface Area m^2/g		Particle Size mm	Powder Density g/cc	
		As Rec'd	Powdered	As Rec'd	Powdered		Apprt	Tap
BBB	22323-30	2.32	2.26	15.2	8.3	0.06*	0.20	0.27
PBI	P915A	0.90	0.93	0.22	0.24	0.02	0.59	0.84
PBI	21684-12	0.59	-	8.5	-	0.01	0.48	0.71
BBB/PBI Coppt.	26085-12	-	-	-	-	0.047*		

*Very broad range of sizes.

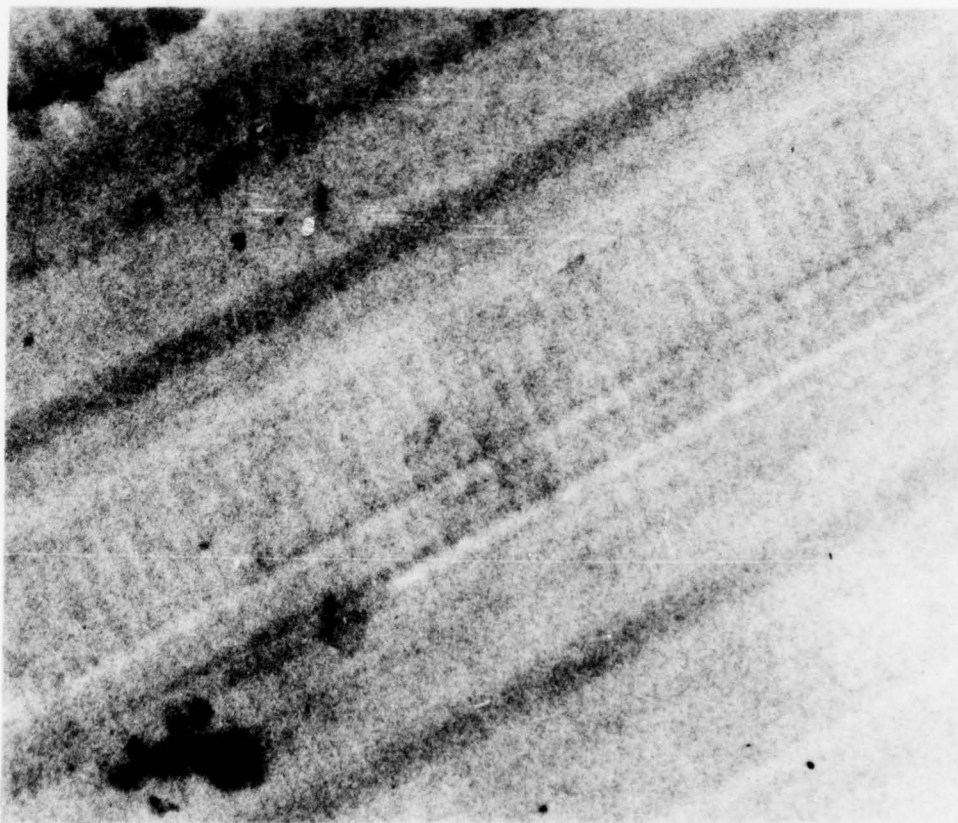**Fig. 1a. (200X)** SEM: BBB Polymer Particle
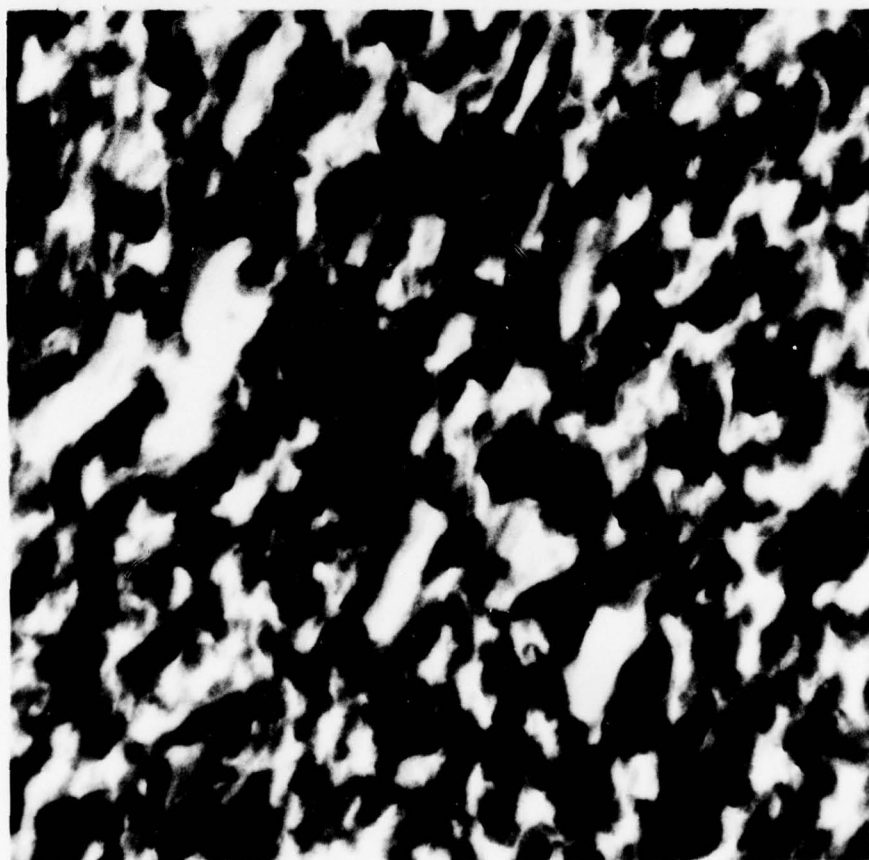
Fig. 1b. (18,400X) TEM: Thin Section BBB Polymer Particle

6.

Fig. 2a. (1000X) SEM: 0.9 I.V. PBI

Fig. 2b. (7000X) TEM: 0.9 I.V. PBI

higher surface area indicating a porous sample. This too is indicated
by the SEM (Figure 3a). Transmission electron micrographs of these
two powders (Figures 2b and 3b) show the 0.90 I.V. material to be
featureless, whereas the 0.59 I.V. polymer has a highly nodular appear-
ance. This probably arises from the fact that, by x-ray diffraction, the
lower I.V. material appears to be quite crystalline.

Only particle size was measured for the co-precipitated materials and
this was in the same range as that of the other materials. Optical
microscopic examination of the co-precipitate (Figure 4) showed that
the particles were quite dense.

B. Mixing

Dry blends of the powders were prepared by tumbling a mixture of the
component polymers for several hours. The co-precipitated material
was prepared by dissolving 8 gms of BBB and 2 gms of PBI in 1000
mils of 100% H_2SO_4 under nitrogen at room temperature for 5 hours
with constant stirring. After solution of the polymers, 3,000 ml. of
methanol was then added slowly with constant agitation to the mixture
surrounded by a cold water bath. The precipitated BBB/PBI blend
was filtered and washed successively with dilute ammonium hydroxide,
water and methanol. The fine particles were dried in air for 72 hours
and then under vacuum for 5 hours at 100°C. A yield of 9.5 gms of the
blend was obtained.

C. Pressing and Testing

The samples were prepared as 1 inch discs, about 0.05 inch thick, by
vacuum hot pressing in the Astropress. With either the blended powder
or the co-precipitate, 0.875 gms of the mixture were loaded into a one-
inch diameter single acting die. To avoid problems of the discs sticking
to the die, the die surfaces were sprayed with Freekote - a mold release
agent. The mold was then placed in the press and a load of 6,000 lbs.
applied while the sample heated up to the desired temperature. When
this temperature was reached, the load was increased to the pre-
determined value and held for the desired time. The sample was then
cooled, under pressure, to about 275°C before being removed from the
press.

To obtain pieces suitable for testing, the discs were cut on an Imanco
Micro-Slice using diamond loaded saw blades. Two 1/4" wide bars were
cut from each disc. With this width, the maximum length of the bars
was about 0.8". In general, good unchipped bars were obtained. However,
with the pure BBB and with the co-precipitated material, difficulties
were experienced in cutting satisfactory specimens. Smaller pieces were
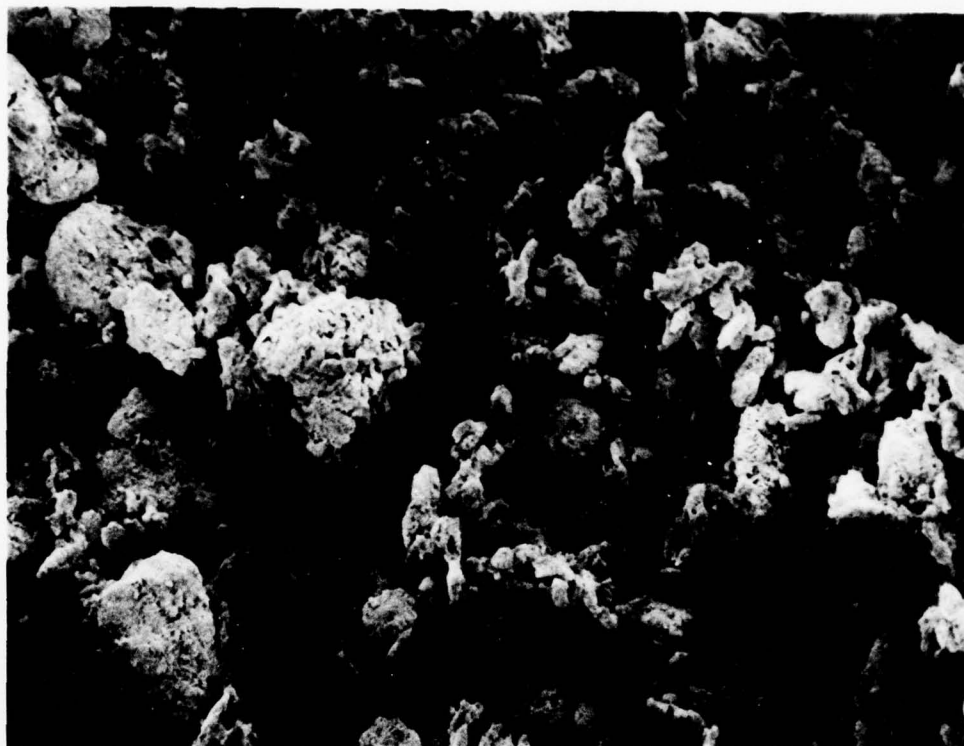
Fig. 3a. (1000X) SEM: 0.59 I.V. PBI
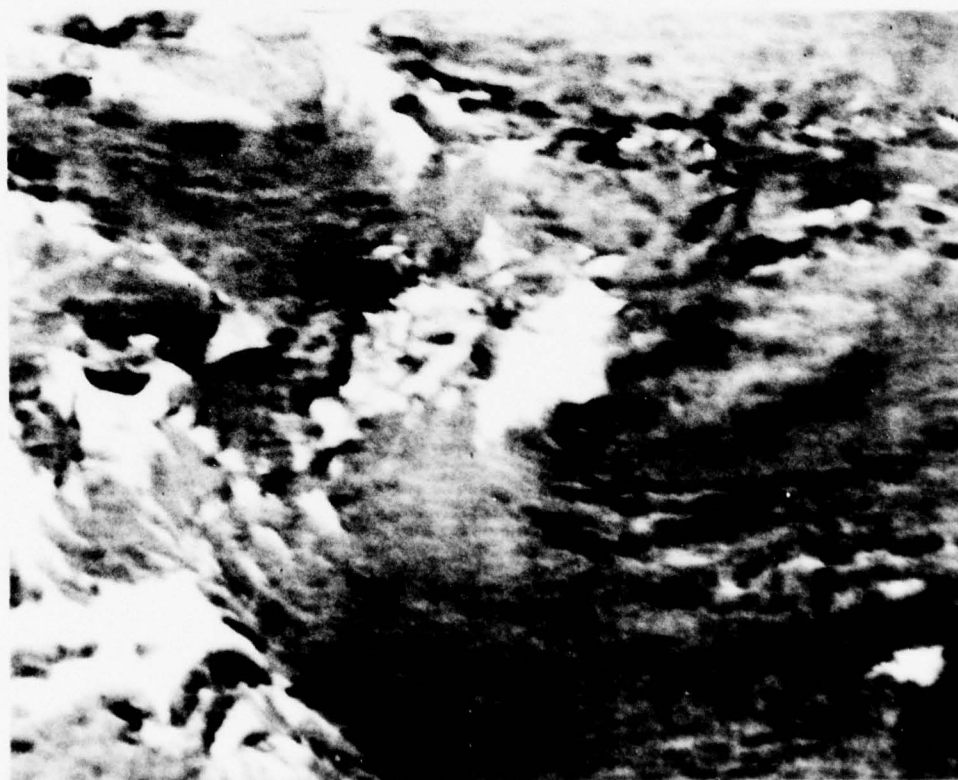
Fig. 3b. (22,000X) TEM: 0.59 I.V. PBI

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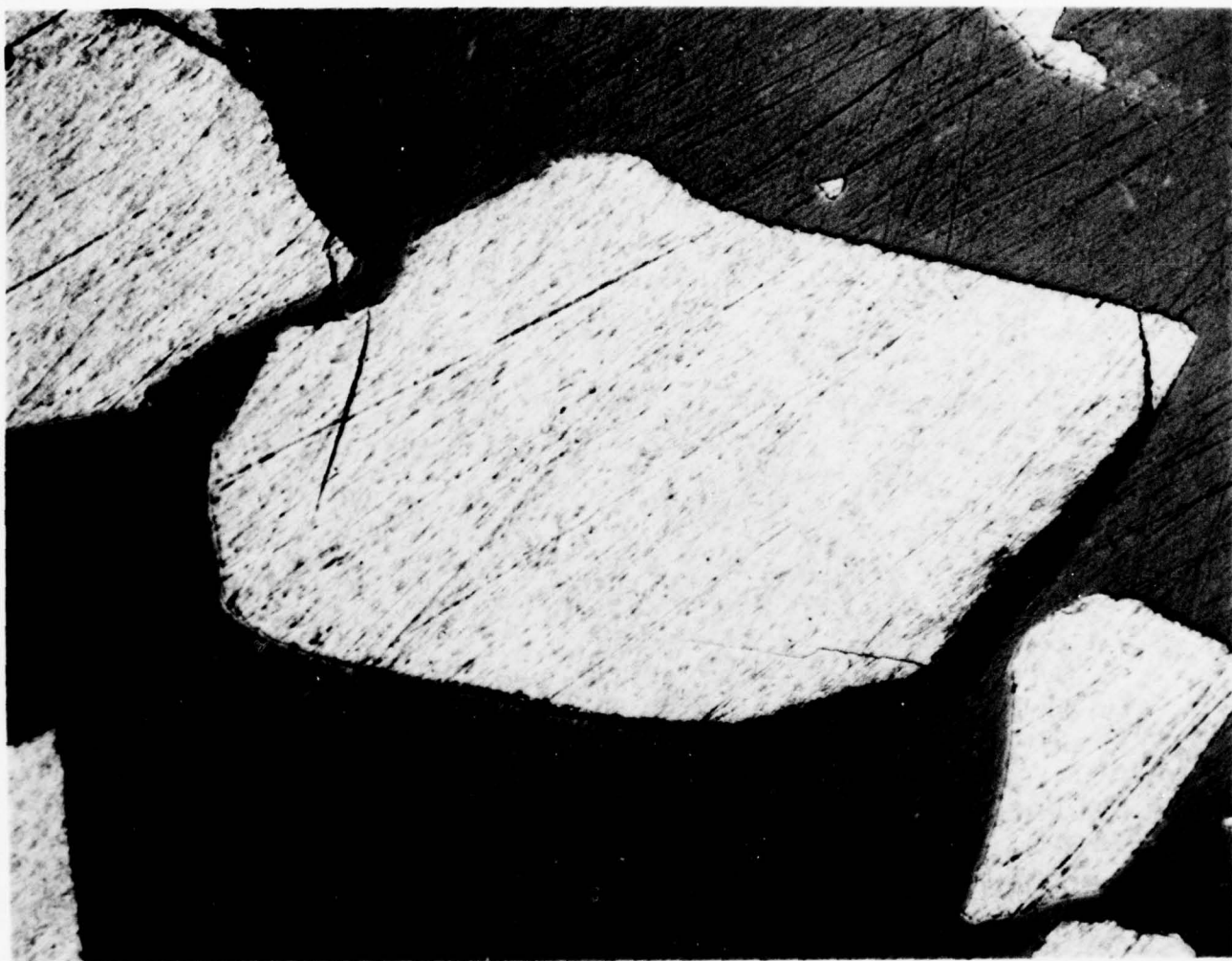
Fig. 4. **(200X)** Optical Micrograph: Co-precipitated BBB/PBI

10.

also cut for the TMA and x-ray study.

Testing was carried out using the ASTM 70 standard test for flexural modulus and strength. The 0.05" thickness was chosen to give a 16:1 or greater aspect ratio for the maximum bar length of 0.8".

D. X-ray Diffraction

Wide and low angle x-ray studies were carried out photographically on several of the molded discs. The wide angle studies were made on standard flat plate cameras. The low angle studies used pinhole collimated cameras mounted on a high intensity rotating anode generator. Intensities of some of the wide angle patterns were measured on a Joyce Loebel microdensitometer for comparisons of orientation to be made. The scans were made parallel and perpendicular to the thickness of the disc and the ratio of peak intensities calculated.

E. Microscopy

For optical microscopy, pieces of the disc were embedded in Buehler Epoxide Resin (20-8130-032) with Buehler Epoxide Hardener (20-8132-009), using a 5:1 mixture ratio for room temperature hardening, and then polished to reveal a cross-section through the thickness of the disc. Standard polishing procedures were used, i.e. grits 240, 320, 400 and 600 successively followed by final polishing with 1μ and 0.3μ Alumina powder. The polished samples were examined in a Leitz microscope using bright field vertical illumination.

For transmission electron microscopy, pieces of the samples were embedded in Maraglas resin and cured overnight at 60°C. Sections were cut at room temperature on an LKB III ultra-microtome using a diamond knife. The sections were examined in a Siemens Elemiskop I transmission electron microscope.

The scanning electron microscopy studies were made in fractured samples, which had been coated with gold to minimize charging effects, in a scanning electron.

F. Thermal Studies

Thermal expansion was measured on a duPont Thermo-mechanical analyzer set for measuring change in thickness. The samples used were cut with the micro-slicer so that change parallel and perpendicular to the thickness could be monitored. Calorimetric studies were made using a duPont differential scanning calorimeter.

11.

SECTION III

RESULTS AND DISCUSSION

A. Results

1. Mechanical Properties

Strength and modulus values obtained for various processing conditions are plotted in Figures 5 to 8 and in Table II and III. Figures 5 and 6 show the effect on modulus and strength of changing the ratio of BBB/PBI at constant processing conditions (475°C, 20,000 psi, 20 minutes). It can be seen that the modulus changes by a factor of 3 between pure BBB and pure PBI with the most rapid increase being between 0 and 50% PBI. There is a much larger increase in strength (about 10 fold) with the change being almost linear with composition for the 0.93 I.V. PBI. The 75% level of the 0.59 I.V. PBI shows a rather low strength but the possibility that this is an artifact cannot be ruled out.

Figures 7 and 8 show the effect on modulus and strength of varying the temperature while keeping the composition constant (80% BBB/20% 0.59 I.V. PBI, 20,000 psi, 20 minutes) together with results on pure BBB. They show that the modulus and strength of the blend is greater than that of the pure BBB at all temperatures up to about 500°C when the properties become indistinguishable.

In Tables II and III, two point comparisons of the effect of dwell time and load are given. Increasing the dwell time increases both strength and modulus in all cases except for the modulus of the pure BBB at 475°C which falls slightly. Increasing the load leads to a decrease in properties except for the modulus of 0.93 I.V. PBI blend.

Table IV lists results for the co-precipitated materials. These samples were very fragile and it was difficult to cut good test specimens from them. Comparison of the modulus values with those of the pure material or blends show that the moduli are at the level of the blends, e.g. $0.5x10^6$ psi for 475°C and 10,000 psi. However, the strengths are close to the values exhibited by the pure BBB in agreement with the difficulties encountered in cutting the samples. Again poorer properties were found for the higher pressure level.

2. X-ray Diffraction

Wide angle x-ray diffraction of the pure BBB before and after pressing showed two very diffuse reflections with the inner one being at about 8.0Å and the outer one at 3.5Å. In the sample which had been pressed
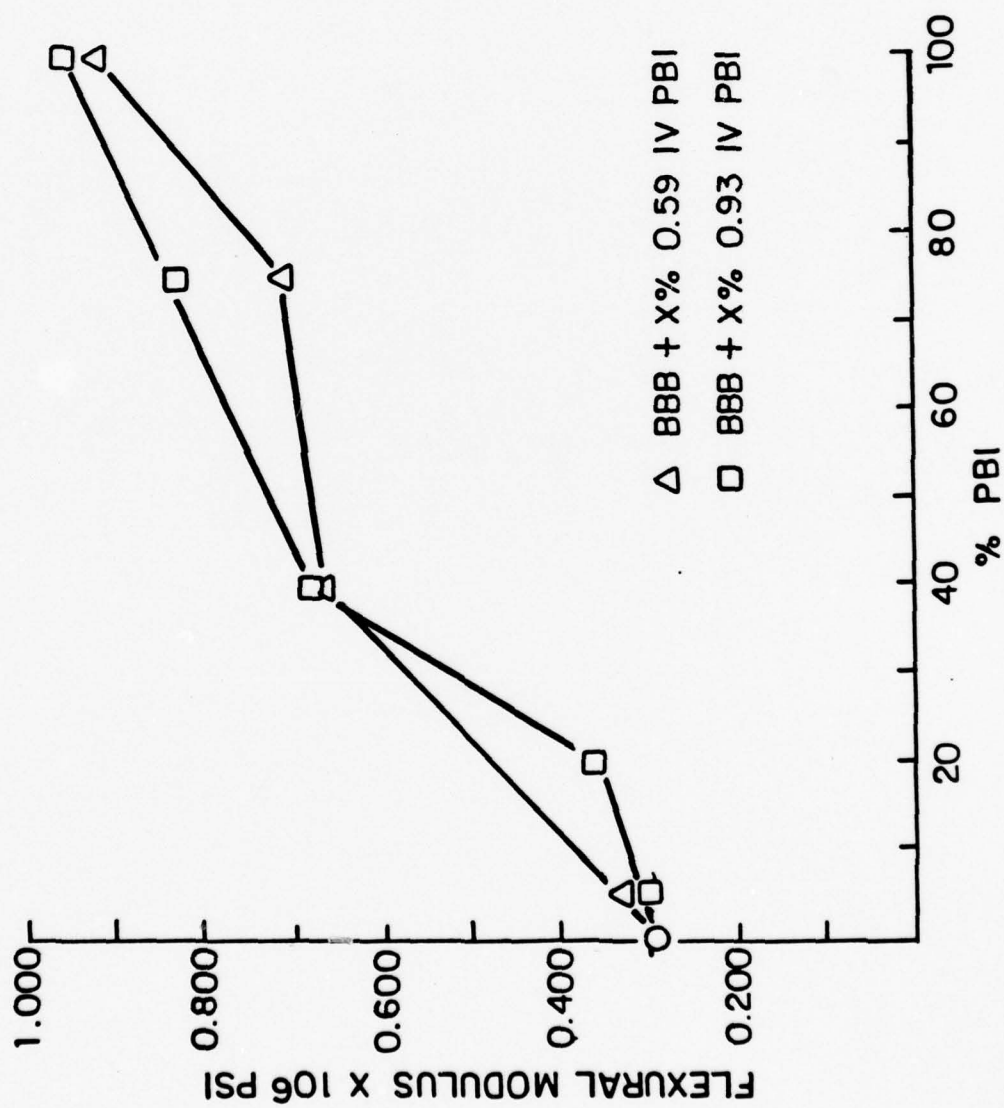
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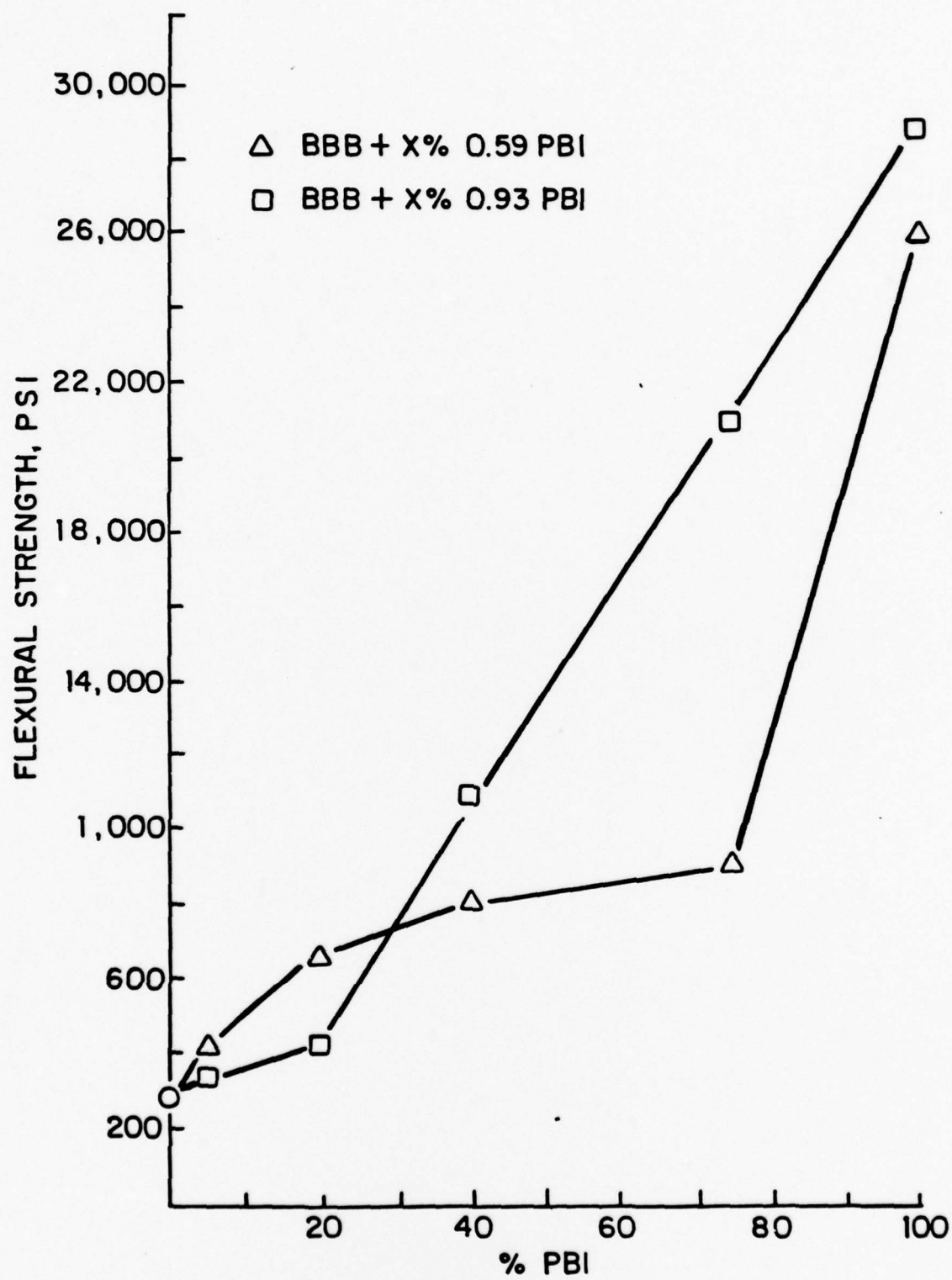Fig. 5. Modulus vs. Composition of BBB/PBI Polymer Alloys

△ BBB + X% 0.59 IV PBI

□ BBB + X% 0.93 IV PBI

% PBI

FLEXURAL MODULUS X 10⁶ PSI

Fig. 6. Strength vs. Composition of BBB/PBI Polymer Alloys

FLEXURAL MODULUS X 10⁶ PSI

0.800

0.600

0.400

0.200

100   200   300   400   500   600

TEMPERATURE, °C
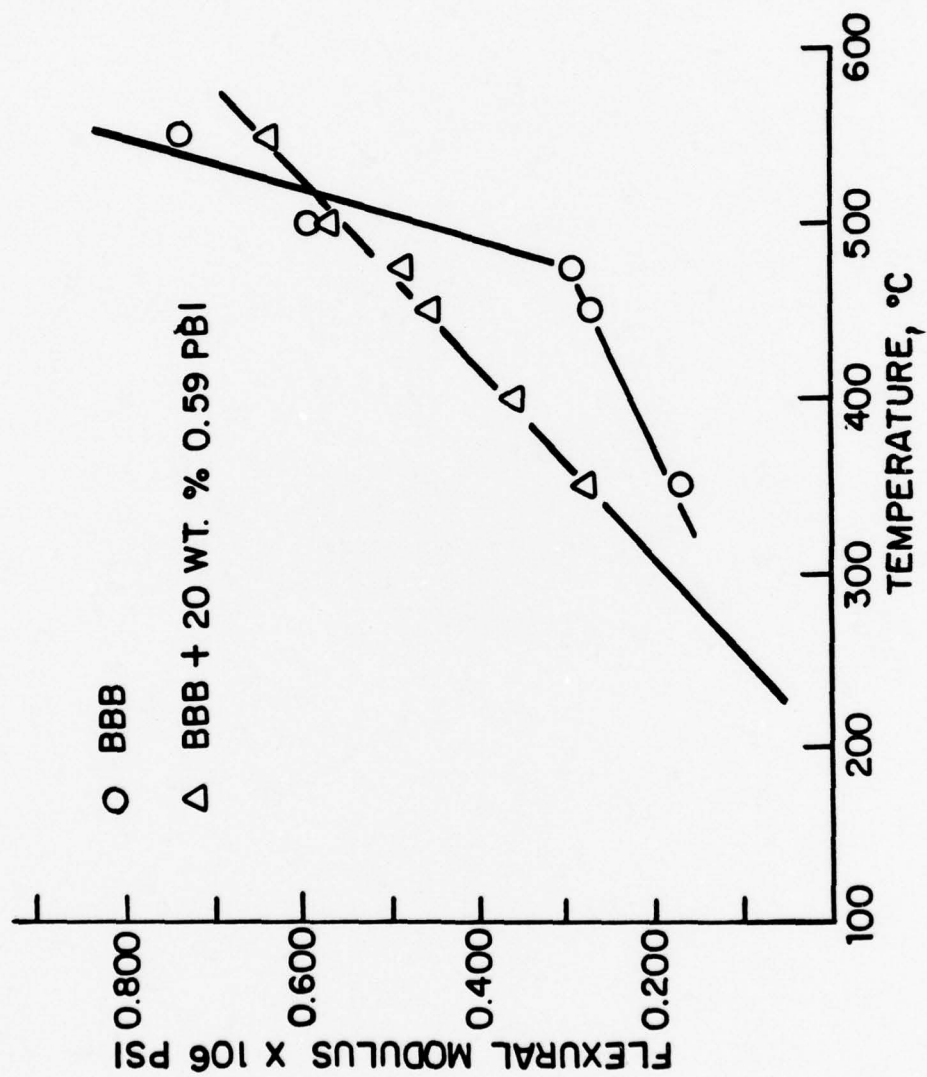
O BBB

△ BBB + 20 WT. % 0.59 PBI

Fig. 7. Modulus vs. Processing Temperature of BBB/PBI Polymer Alloys
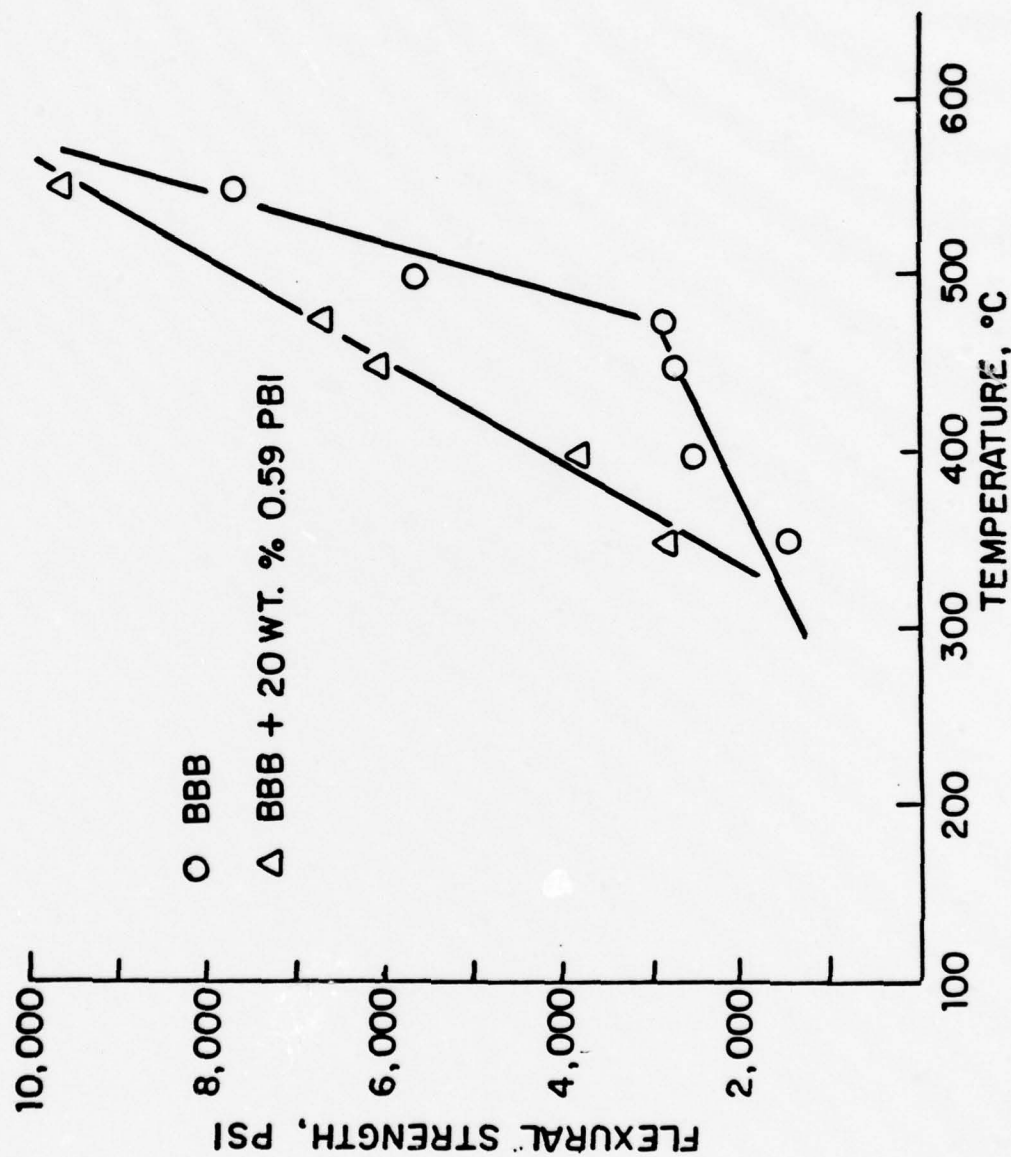
15.

Fig. 8. Strength vs. Processing Temperature of BBB/PBI Polymer Alloys

TABLE II

MODULUS AND STRENGTH VS. TEMPERATURE AND TIME FOR BBB/PBI BLENDS

		Temperature (°C)			
		400°		475°	
Polymer	Time (min.)	Modulus psi	Strength psi	Modulus psi	Strength psi
BBB	5	130,000	1400	350,000	2600
	20	260,000	2500	300,000	2900
BBB/0.59 PBI 80/20	5	260,000	3300	350,000	3600
	20	360,000	3900	540,000	7300
BBB/0.93 PBI 80/20	5	190,000	2000	340,000	3600
	20	260,000	2900	400,000	5300

TABLE III

MODULUS AND STRENGTH VS. APPLIED LOAD

Polymer	Load (lbs.)	Modulus (psi)	Strength (psi)
BBB	10,000	290,000	2800
	20,000	210,000	2400
BBB/0.59 PBI 80/20	10,000	530,000	7300
	20,000	420,000	5100
BBB/0.93 PBI 80/20	10,000	400,000	5300
	20,000	430,000	4200

TABLE IV

PROPERTIES OF CO-PRECIPITATED 80/20 BBB/PBI BLEND

	Load Pressure (lbs.)			
	10,000		20,000	
Temp (°C)	Modulus	Strength	Modulus	Strength
	(psi)		(psi)	
350°	-	266	298,000	724
475°	519,000	3430	342,000	1750
550°	426,000	3530[1]	(2)	

(1) Best value
(2) Samples fractured in cutting

19.

at 20,000 psi and 475°C, the 3.5Å ring showed some orientation indicating a planar orientation, i.e., one in which the appropriate reflecting planes are aligned perpendicular to a particular axis, in this case, the compression axis. The 8.0Å ring, on the other hand, showed no preferred orientation. In addition, the pressed sample exhibited a sharp unoriented reflection, at about 3.12Å.

The 0.93 I.V. PBI showed only a very diffuse ring at about 4.7Å before and after pressing with no orientation effects. The 0.59 I.V. PBI was highly crystalline (see list of spacings in Table V) both before and after pressing. This again showed no orientation effects on treatment.

X-ray patterns from the blends essentially showed a superpositioning of these observations. With BBB and 0.93 I.V. PBI, only the BBB reflections were observed, with the orientation similar to that for straight BBB and with the additional sharp relfections at 3.12Å. With BBB and 0.59 I.V. PBI, the crystalline PBI was observed super-imposed in the BBB patern.

Different treatment conditions (temperature, time, pressure) gave almost identical x-ray patterns, the only difference being the intensity of the sharp additional BBB reflections. At 400°C and 5 minutes, the 3.12 Å reflection was barely visible. At 475°C for 20 minutes, the 3.12 Å reflection was strong and some additional reflections at about 2.2 Å were observed.

The co-precipitated BBB-0.59 I.V. PBI differed in that the orientation of the BBB 3.5Å reflection was much less. Furthermore, no extra crystalline reflection appeared after the heat treatment and no PBI reflections were observed.

Only some of the early samples were examined at low angle. The straight BBB sample was compared with BBB/PBI blends. In each case, there was a strong, diffuse central scatter which usually can be associated with voids. The scatter was asymmetrical, being elongated preferentially along the compression axis, i.e. taking into account the reciprocal relationship in scattering, this could be due to voids elongated in the plane of the flat test piece. The intensity and extent of the scattering increased with temperature and time suggesting that the voids get smaller and/or some degradation is occurring giving rise to additional small voids.

TABLE V

SPACINGS FOR 0.59 I.V. PBI

No.	Spacing $\overset{\circ}{A}$	Comments
1	6.32	Very strong
2	4.93	Doublet weak/medium
3	4.17	Strong
4	3.75	Strong
5	3.01	Medium

3. Optical Microscopy

Pure BBB samples treated at 350, 450 and 550°C were examined (Figure 9 of a 450°C sample is representative). Each showed a texturing which appeared to correspond with the original particles with a flattening of the texture perpendicular to the compression axis. The 550°C sample appeared to be better compacted than did the 350°C sample. The color of the samples also changed with temperature being golden for 350°C and almost silver for the sample tested at 550°C.

Pure 0.59 I.V. PBI showed a fine texturing, about 10μ as so, which corresponded to a slight color difference within the sample. The samples were silver-colored in general. Comparison of the pressed sample with the SEM of the powder suggests that the mottling corresponds to the finest particles visible in the SEM. It is to be noted that the particle size analysis indicates about 10μ.
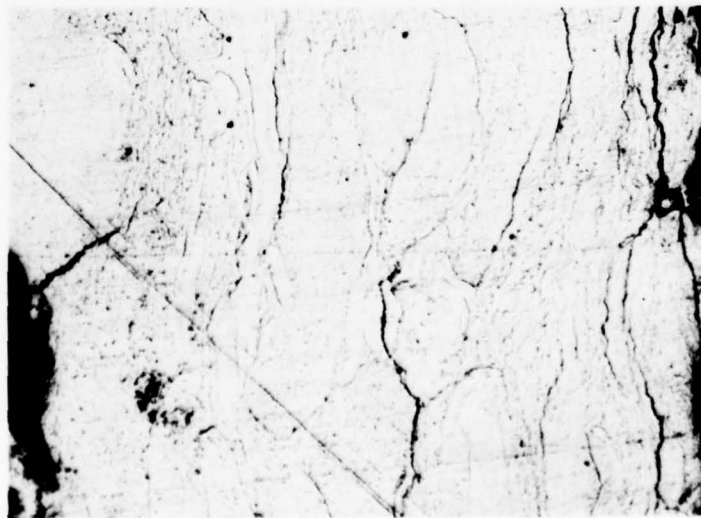
Pure 0.93 I.V. PBI has a much coarser texturing than is the case for the 0.59 PBI large particles. The 0.93 I.V. PBI particles were of the order of 200μ and appeared to be cemented together (Figure 11) by a darker material. Again, comparison with the SEM of the untreated powder shows that the large particles are of the same order of size as the large particles in the powder. In this case, the smaller particles appear to have fused together to form the darker phase.

In the BBB/PBI blends, two distinct phases were apparent, with the BBB having a golden tinge and the PBI a silvery hue. In the optical micrographs (Figures 12 and 13) the PBI shows up as the darker phase. At low concentrations of BBB (Figures 12a and 13a), the PBI phase is continuous and has the texture of the corresponding pure material. At high BBB concentrations, the BBB phase is continuous (Figures 12c and 13c), again with the texture of pure BBB. The transition between continuous phases occurs at about 40% (Figures 12b and 13b).
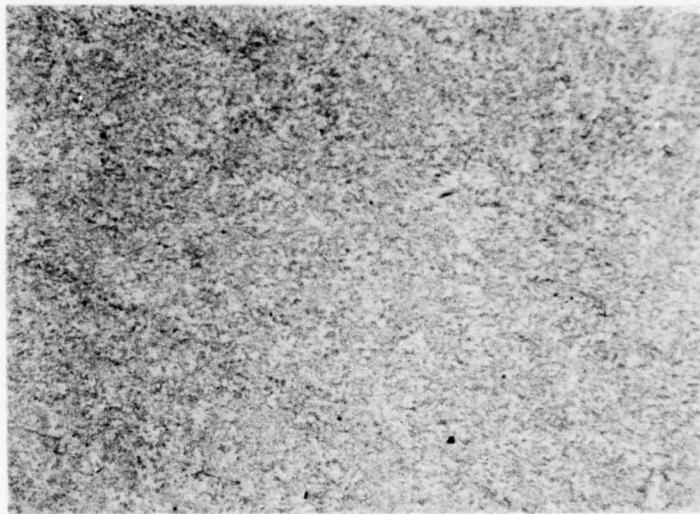
Mixtures of BBB/0.59 I.V. PBI were processed at 350°, 450°, and 550°C. As with the pure BBB, the color of the BBB changed giving less contrast between the BBB and PBI phases. It also appeared as if the total area of the darker, PBI-rich phase, was greater as the temperature was increased.

When the two polymers were co-precipitated, the optical micrographs confirmed that a true co-precipitation had taken place. The two phases could be distinguished in individual particles with the PBI appearing as silver flecks in the golden BBB matrix. The size of the PBI inclusions was of the order 1 - 5μ.
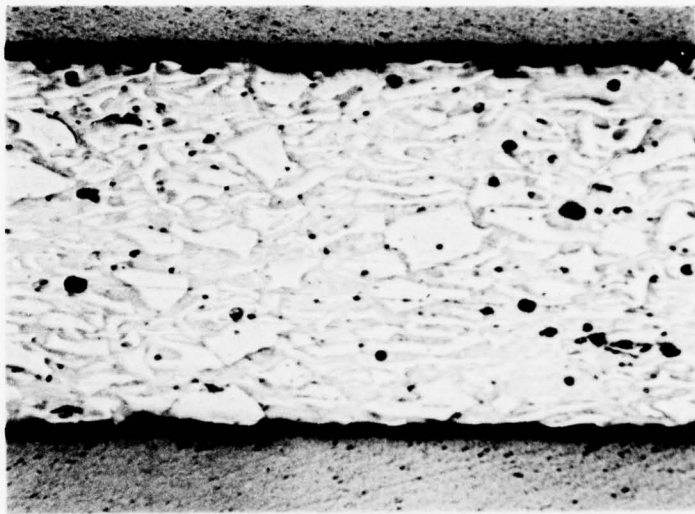
Fig. 11. (50x) Optical Micrograph:
Pure 0.93 I.V. PBI
Pressed @ 450°C, 20,000psi, 20 min

Fig. 10. (200x) Optical Micrograph:
Pure 0.59 I.V. PBI
Pressed @450°C, 20,000psi, 20 min

Fig. 9. (200x) Optical Micrograph:
Pure BBB
Pressed @450°C, 20,000psi, 20 min
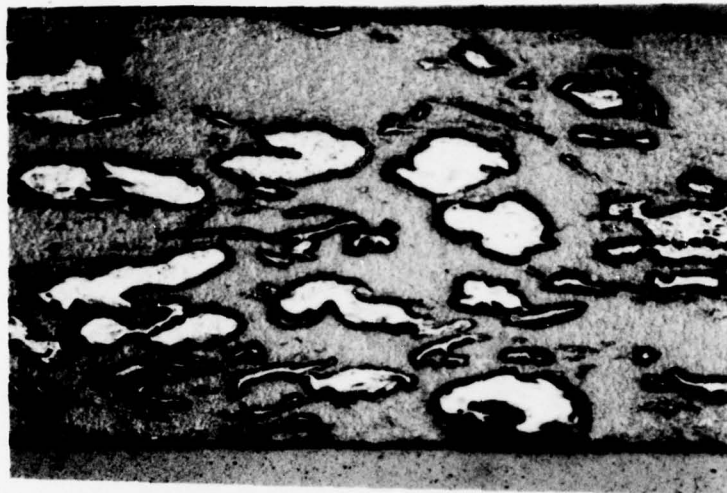
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OPTICAL MICROGRAPHS
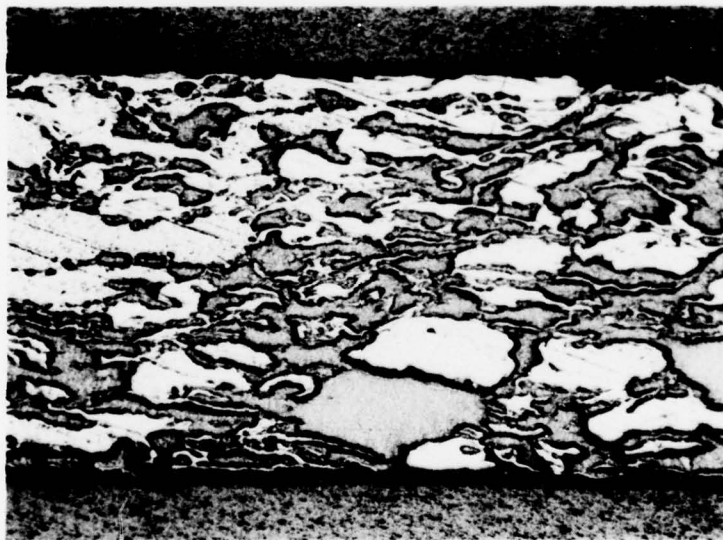
Fig. 12a. (50X) 25 BBB/75 0.59 PBI
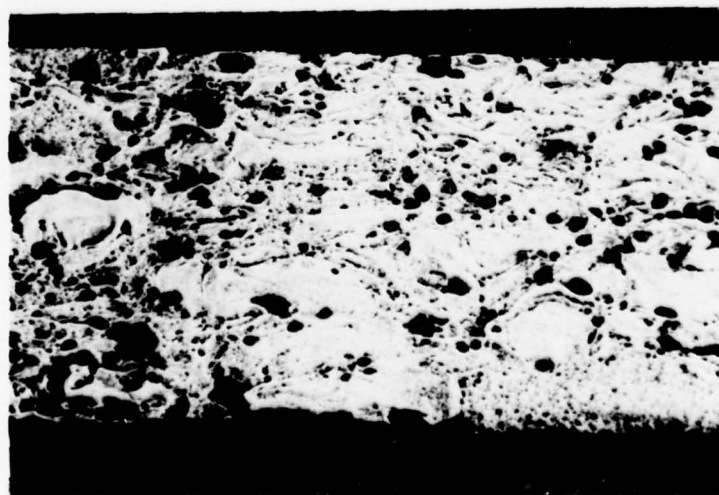
Fig. 12b. (50X) 60 BBB/40 0.59 PBI

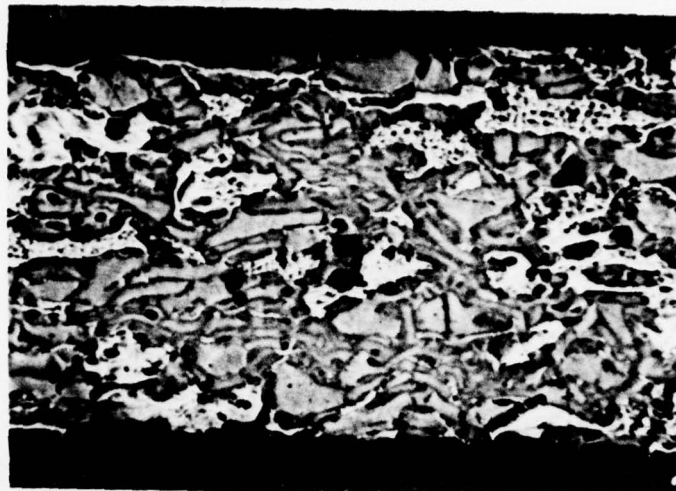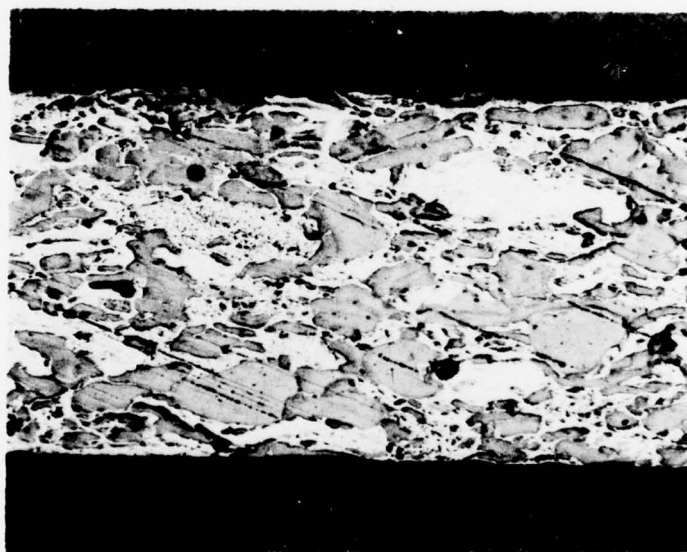**Fig. 12c. (50X)** 95 BBB/5 0.59 PBI
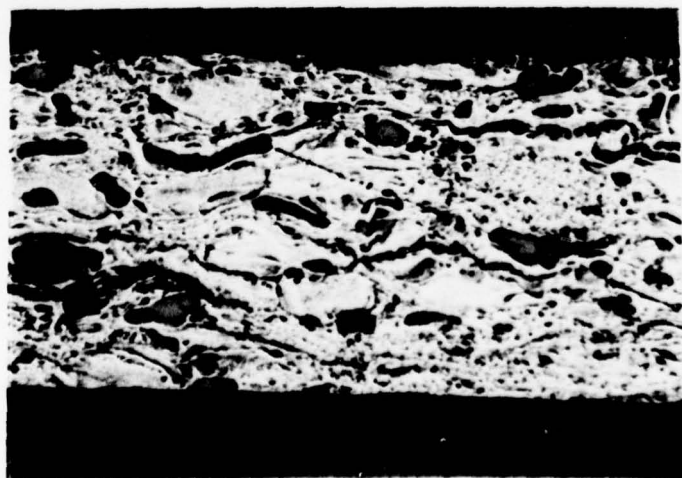
Fig. 13a. (50X) 25 BBB/75 0.93 PBI

Fig. 13b. (50X) 60 BBB/40 0.93 PBI

Fig. 13c. (50X) 95 BBB/5 0.93 PBI

After processing, the boundaries of the individual particles could still be distinguished (Figures 14a and b), with cracks between particles in the lower temperature sample (Figure 14a). At higher magnification (Figure 15a and b), the two phases are still clearly visible, again with the size of the PBI being in the range of a few microns. As with the dry blends, the tint of the BBB changes with processing temperature, becoming more silvery while the total area of the PBI (darker phase in the micrographs) appeared to increase (compare Figures 15a and 15b).

4. Transmission Electron-microscopy

Sections of pressed discs of the pure polymers and blends were examined together with sections of the untreated powders. As already mentioned, there were distinctive textural differences between the three untreated polymers. The BBB had a very open, porous structure, Figure 1b, whereas the 0.93 I.V. PBI was compact and featureless (Figure 2b). The 0.59 I.V. PBI sample had a mottled texture in the size range of a few hundred Angstrom units (Figure 3b).

The pure BBB treated at 475°C, 20 minutes, 10,000 psi (Figure 16) is much more compact and shows a nodular texture in the range of a few 1000 Angstrom units. The 0.93 I.V. PBI remained quite featureless with occassional inclusions, as seen in Figure 17. These inclusions have not yet been identified. In the 0.59 I.V. PBI, the texture observed in the unprocessed material was again apparent (Figure 18).

In the mixture, the individual phases could be detected. Figure 19 is a photomicrograph of an 80/20 BBB/0.59 I.V. PBI blend treated at 475°C, 10,000 psi and 20 minutes. It shows a PBI particle embedded in the BBB matrix and individual particle boundaries of the BBB can be identified. There is also a difference in texture at the lower BBB/PBI boundary but not enough samples have been examined to determine whether this is a real effect or not.

5. Scanning Electron Microscopy

Fracture surfaces of some of the initial samples were examined using the scanning electron microscopy (Figure 20a and b). In general, these showed a layered structure with the layers being parallel to the surface of the discs. The pure BBB samples (Figure 20a) showed a "clear" break in which fracture appeared to have taken place between flattened particles. The samples containing 20% 0.59 I.V. PBI showed areas in which fibrils appeared to have been drawn out (Figure 20b) indicative of the better cohesion exhibited by these samples.
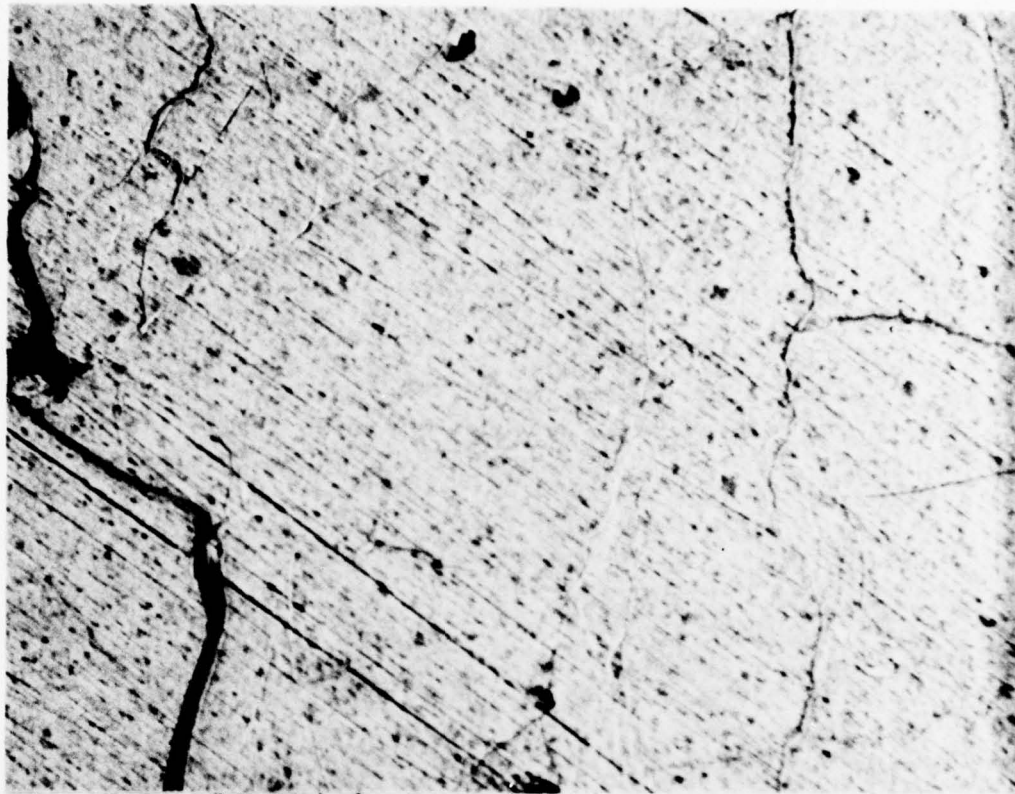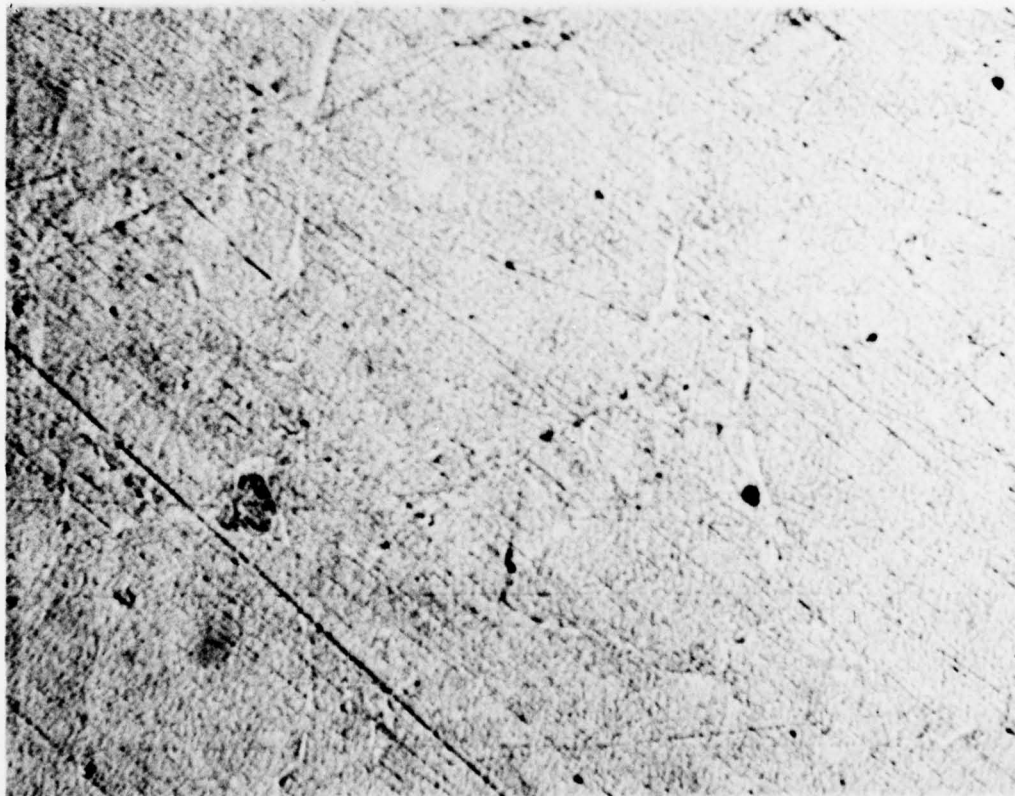
Fig. 14a. (200X)
Pressed @ 350°C, 10,000 psi, 20 min

Fig. 14b. (200X) Pressed @ 475°C, 10,000 psi, 20 min

Fig. 15b. (500x) Co-precipitated BBB/PBI
Pressed @ 550°C, 10,000 psi, 20 min

Fig. 15a. (500x) Co-precipitated BBB/PBI
Pressed @ 350°C, 10,000 psi, 20 min

28.

Fig. 16. (18,400)

TEM: BBB Pressed @ 475°C, 10,000 psi, 20 min

29.
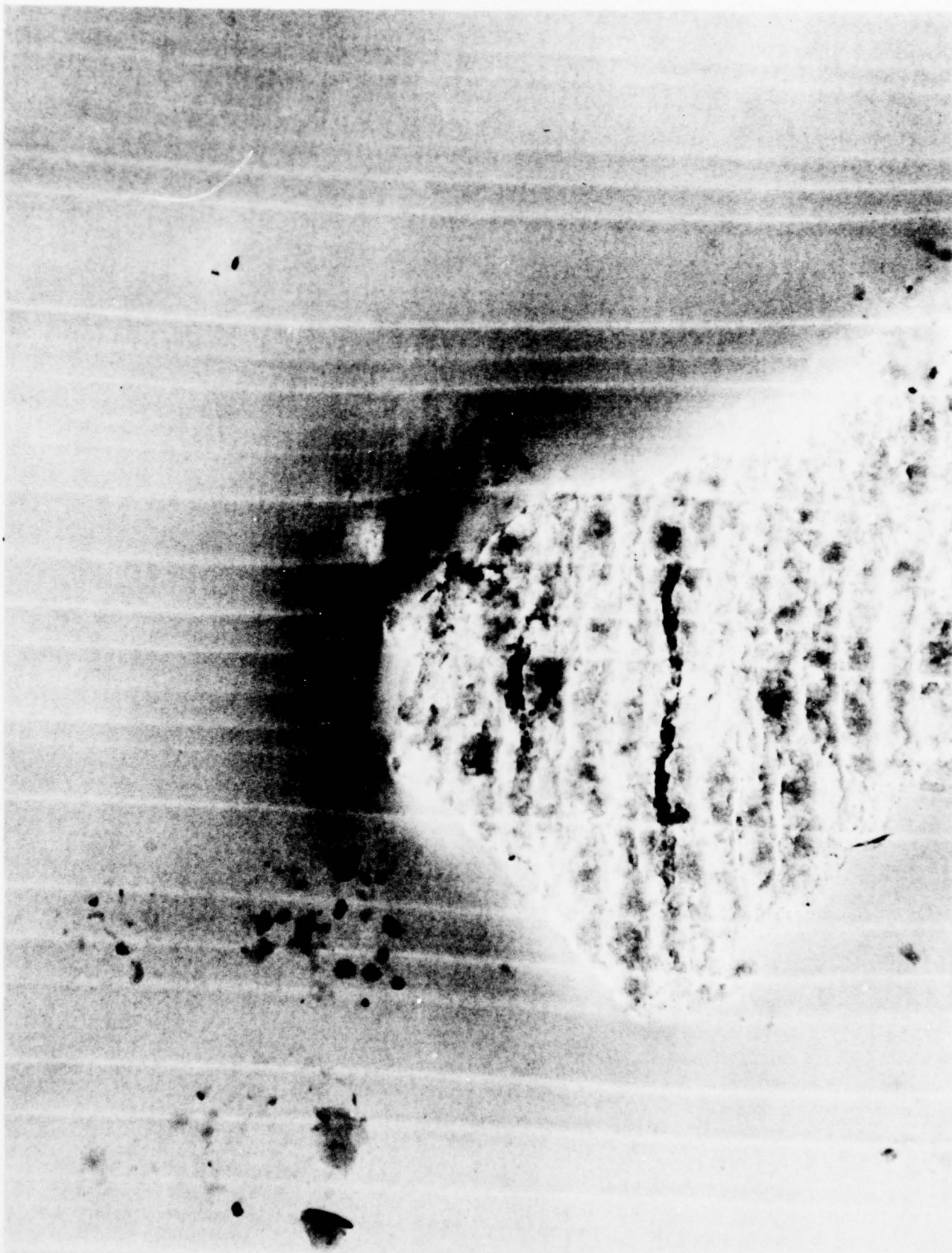
Fig. 17. (51,600) TEM: PBI 0.93 I.V. Pressed @ 475°C, 10,000 psi, 60 min

Fig. 18. (21,600X) TEM: 0.59 I.V. PBI Pressed @ 475°C, 10,000 psi, 60 min
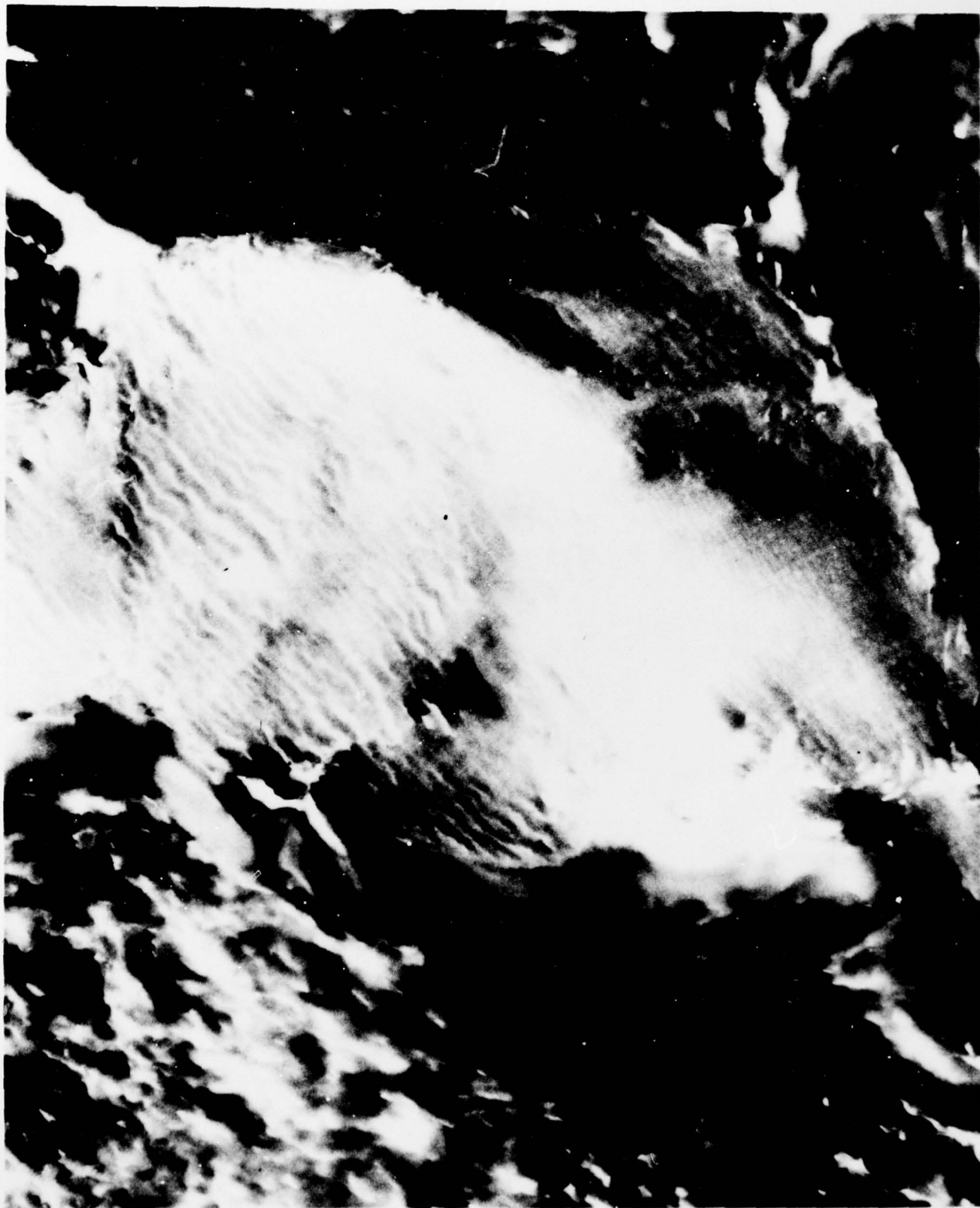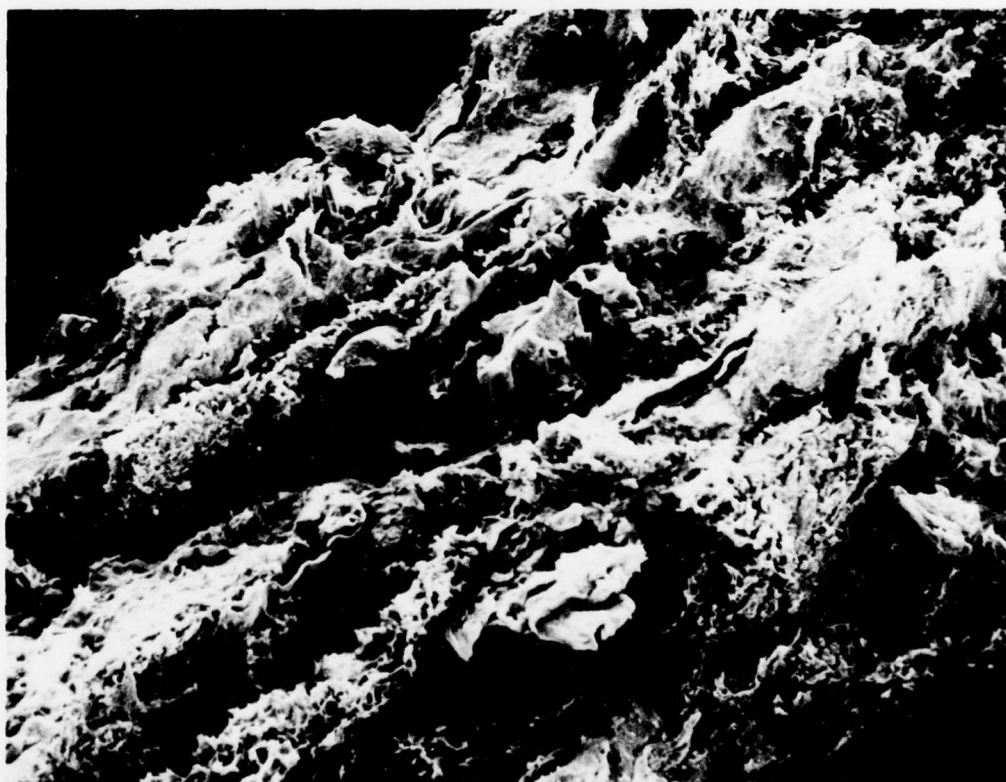
31.

Figure 19. (18,400 X) TEM: BBB/0.59 PBI Pressed @ 475°C, 10,000 psi, 20 min

32.

Fig. 20a. (110X) SEM: Fractured BBB Disc Pressed @ 475°C, 20 min

Fig. 20b. (110X) SEM: Fractured BBB/ 0.59 PBI
Disc Pressed @ 475°C, 20 min

33.

6. Thermal Analysis

Differential scanning calorimetry curves showed no differences with changes in treatment condition. In each case, there was a peak at about 100°C due, probably, to water being driven off followed by a very broad exotherm which peaked at about 400°C.

The thermal expansion was measured in two orthogonal directions: namely, in the thickness direction and in the plane of the disc (Table VI). The thickness increased quite slowly up to about 400°C, at which point the change was much more rapid with increasing temperature, reaching a peak at about 600-650°C. The total expansion at 600°C was measured for both directions and the results are listed in Table VI. The expansion in thickness was generally much greater than the change in width. The change in thickness was lower for the blends, at similar processing conditions, than for the pure BBB. Increasing time and pressure also tends to decrease the expansion. No clear trend of expansion versus processing conditions was observed for the width.

B. Discussion

The results on the change of mechanical properties with composition and processing conditions confirm that the blending of even 20% of PBI with BBB has a marked affect on the properties which can be achieved. For example, with the 0.59 I.V. PBI, a similar modulus level was found at 350°C for the 80/20 blend as was exhibited by the pure BBB at about 475°C. Furthermore, the variation of properties with processing temperature also shows that both the modulus and strength of the pure BBB increases only slowly so that at a processing temperature of 475°C for the blend, the modulus of the 0.59 I.V. blend is approximately 0.5×10^6 psi compared to 0.3×10^6 psi for the pure BBB. The strength of the blend is also much higher, being 7.0×10^3 psi compared with 3×10^3 psi for the pure material. However, above 500°C the properties of the pure BBB increase rapidly with processing temperature, reaching a similar level to that of the blend at 550°C.

The pure PBI, on the otherhand, shows very much better properties than either the blend or the BBB when processed at 475°C. The micrographs and x-ray data show that this is a bonding effect as opposed to a total melting of the polymer, e.g. the crystallinity of the 0.59 I.V. and the 0.93 I.V. materials, which are completely different, do not change during the processing.

Taken together, these results suggest there are at least two temperature activated processes which lead to the bonding together of the polymer

34.

TABLE VI

THERMAL EXPANSION OF BBB AND BLENDS BETWEEN ROOM TEMPERATURE AND 600°C

Polymer	Temperature (°C)	Time (min)	Load (lbs.)	Coefficient of Thermal Expansion ($°C^{-1} \times 10^5$)	
				Thickness	Width
BBB	475°	5	10,000	10.7	0.4
	475°	20	10,000	10.2	0.2
	475°	20	20,000	5.1	2.3
BBB/0.59 PBI 80/20	475°	5	10,000	7.1	0.4
	475°	20	10,000	7.0	0.8
	475°	20	20,000	3.8	0
BBB/0.93 PBI 80/20	475°	5	10,000	6.4	1.6
	475°	20	10,000	2.1	0
	475°	20	20,000	2.3	1.9

particles. In the pure BBB, the initial effect is a compaction of the open porous material, leading to the orientation effects observed by x-ray but not to any marked degree of bonding. Above about 500°C, however, bonding together of the polymer occurs giving rise to the improvement in properties. This process probably also accounts for the similarity in properties between BBB and the blends above 500°C.

In the pure PBI, no similar compaction occurs since the material is initially more dense. However, a very distinct bonding occurs at 475°C, the only temperature tested, giving rise to the high modulus and strength of these materials.

The results with blends do not clearly indicate whether the third process, BBB/PBI intereaction is occurring. The fact that the properties are substantially improved at the 20% PBI level may be taken as some evidence for this since it is not until the 40% PBI level that a PBI matrix is set up. More convincing is the optical micrograph evidence which shows that the PBI-rich phase grows with increasing processing temperature. Finally, the higher moduli exhibited by the co-precipitated material could imply that a PBI-BBB interaction was occurring within the particles. The low strengths of these latter materials probably arises because the interparticle boundaries are principally BBB/BBB.

The positive effect of increasing time, particularly at higher temperature (Table II) is consistent with a temperature-activated process and suggests that temperatures greater than 400°C are preferred. The effect of increasing pressure is to raise the glass transition temperature. The lower properties at higher processing pressures may be accounted for by the decrease in mobility of the molecules which serves to suppress the temperature-activated processes. This means that a balance may have to be struck between compaction, which requires a high pressure, and bonding which progresses more readily at a lower pressure.

Thus, the studies so far have indicated the possibility of three temperature-activated bonding processes occuring in the high temperature-high pressure treatment of BBB-PBI blends. Although effects can be observed in dry blended materials at temperatures as low as 350°C and with PBI levels of 20% it is clear that for optimization of the processes which occur at higher temperatures, different PBI levels and other mixing conditions should be utilized. Preferably temperatures above 400°C, pressures of about 10,000 psi, and pressing times of the order of 20 minutes are indicated. Both pure BBB and PBI should be looked at further in order to identify homo-polymer mechanisms. Similarly, dry blends and co-precipitated materials need to be examined to look for inter-polymer

reactions. The two methods of blending will give rise to very different contact areas between the two polymers and hence change the relative values of the various interactions which occur in a blend. Besides continuing the microscopic studies on the blends, the techniques to be used to identify the molecular processes which occur will include infrared analysis, thermal-spectrometric analysis, electron-proton resonance analysis and such other physical techniques as measurement of intrinsic viscosity, thermo-mechanical analysis and dynamic mechanical spectroscopy. The use of model compounds may also be desirable to identify more clearly particular reaction mechanisms which may be suspected.

SECTION IV

REFERENCES

(1) AFML-TR-67-172 "Thermally Stable Polymeric Fibers."

(2) AFML-TR-73-217 "Exploratory Development of the Investigation of Methods to Process BBB, BBL and Related Polymers," October 1973.

(3) A proposal to "Study the Processing Mechanisms, Structure and Morphology of High Temperature Polymeric Alloys," submitted to AFOSR December 1975.

SECTION V

LIST OF PERSONNEL

During the course of this first year's effort on this project, the following members of the Celanese Research Company professional scientific staff have contributed to the progress of the investigation:

Ian L. Hay - Research Associate, (Principal Investigator)
Jay R. Shaner - Research Scientist
M.A. Sieminski - Research Associate
L. Sawyer - Senior Research Scientist

At the Celanese Research Company, the work was performed within the Materials and Engineering Research Department under the direction of Dr. G. Farrow, Research Director and managed by Dr. C.V. Evins, Manager, Physics Section. Contract Administration was the responsibility of Dr. Joseph R. Leal, Senior Staff Associate.